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Short communication

Effect of salt addition on hydrothermal carbonization of lignocellulosic biomass

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ABSTRACT

As a renewable non-food resource, lignocellulosic biomass has great potential as an energy source. When pretreated by hydrothermal carbonization, the resulting biochar (or hydrochar) is hydrophobic and of higher energy density. Addition of ionic salts to this high pressure aqueous pretreatment reduces reaction pressure. Ca propionate, Ca acetate, Mg acetate, Ca lactate, Li chloride, Ca chloride, and Ca formate were tested in hydrothermal carbonizations at 260 °C for 5 min. Ca chloride and Ca lactate were found to be Ca salts whose addition increases HHV and which decrease the pretreatment pressure. Biomass pretreated with chemical addition of selected salts may have desirable properties when co-fired in existing coal boilers.

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1. Introduction

Producing electrical energy using coal has been customary in countries which possess this fossil fuel. While inexpensive to mine, coal has challenges associated with its use. As a fossil fuel, it is limited in quantity and cannot be used alone indefinitely. In addition, in many parts of the world, coal has high sulfur content, and its burning causes severe pollution problems, such as acid rain, fine particulates, smog, and high ground- level ozone concentration [1,2], requiring use of expensive pollution-control processes. Lignocellulosic biomass is a renewable solid fuel, which typically has very low sulfur and nitrogen, and co-firing with coal has the advantage of reducing the carbon footprint. Co-firing biomass specially pretreated by addition of selected salts may have the further advantage of enhancing combustion and reducing cost of pollution control [3,4].

Challenges in the use of raw lignocellulosic biomass include its wide diversity of form and processing methods, decomposition during the storage necessary due to different harvesting times and locations, transportation problems due to biomass particle size variation, and especially its low fuel value compared to coal. Solutions to the challenges of lignocellulosic biomass use are found in pretreating the raw biomass. Hydrothermal carbonization (HTC), or wet torrefaction, is a promising pretreatment method to improve raw biomass for further use which does not require expensive drying of the raw biomass [5–8].

In the HTC pretreatment, milled biomass is immersed in subcritical water and heated to temperatures between 200 and 300 °C at pressures high enough to maintain liquid water for 1–30 min. HTC removes hemicellulose and some cellulose, leaving high fuel value carbonaceous char as its solid product (biochar) readily made into uniform pellets, which may ameliorate lignocellulosic biomass' low fuel value problem [7,8]. HTC also causes the resulting biochar to be hydrophobic, enhancing its stability when transported or stored in an environment open to the elements [7]. HTC is a high-pressure process, requiring thick reactor walls and arduous safety procedures. Addition of ionic salts to water reduces its vapor pressure, and is one strategy to reduce the cost of HTC pretreatment [6].

In coal furnaces, Ca plays a dominant role in retaining SO_x in the ash that remains after combustion [9]. Ca catalyses the combustion of synthetic chars [10], and greater catalytic effects are observed for calcium compared to magnesium [1]. The reaction scheme for coal with calcium magnesium acetate added has been described [2], but is expensive [11]. Calcium propionate and calcium acetate have also been found to reduce NO and SO_2 in coal fired flue gas [11]. In the present study, various Ca salts, as well as Mg acetate, were added to the HTC process to investigate their effect on pressure reduction during HTC and effect on higher heating value (HHV) and mass yield of the biochar product.

2. Material and methods

As a representative lignocellulosic biomass, loblolly pine was acquired from Alabama, USA. Pine samples were milled to the desired particle size of 14–28 mesh (1.168–0.589 mm in diameter) and dried for 24 h at 105 °C prior to weighing and use in hydrothermal carbonization.

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Ca propionate, Ca acetate, and Ca formate were obtained from MP Biomedicals, LLC (Solon, OH, USA). Mg acetate tetrahydrate, Ca lactate pentahydrate, and Ca chloride were obtained from Fisher Scientific (Fairlawn, NJ, USA). Mg acetate tetrahydrate and Ca lactate pentahydrate are referred to as Mg acetate and Ca lactate, respectively in the remainder of this work for brevity. Li chloride was obtained from Alfa Aesar. Except for runs using Li chloride or $CaCl_2$, 8 g of biomass was used per run. All data reported here are given on a bone dry basis, unless explicitly noted otherwise. All salts, except LiCl and $CaCl_2$, were dissolved by stirring 8 g into 40 g deionized water, so that 1 g of each salt was added per g of pine for a hydrothermal carbonization reaction. For the chloride salts, only 7 g of salt were stirred into 35 g of deionized water, and 7 g of biomass was used instead of 8 g. Reduced amounts of reactants were used because of the space in the reactor taken up by the glass liner used with the chloride salts to prevent pitting in the metal reactor.

Hydrothermal carbonization of loblolly pine was done in a 100-mL Parr reactor at 260 °C for 5 min, with a ratio of water to biomass 5:1. LiCl, $CaCl_2$, Ca lactate, and control (no salt added) experiments were performed and analyzed in triplicate to assess experimental reproducibility. Further details of the experimental method and product characterization are given in Ref. [6]. Time and temperature experimental conditions were different in that heating to 260 °C took 60 min, where the reaction temperature was held for 5 min. The reactants were above 180 °C for approximately 45 min and above 200 °C for about 35 min. Cooling of the reactor interior to below 180 °C in an ice bath took 1 min.

3. Results and discussion

A summary of the experimental results is shown in Table 1 for all chemical additions. The results for the control and for three of the salt additions were run in triplicate and the standard deviation for each result is reported in Table 1. Results shown in the first row are for a control experiment, in which the pine was pretreated in hot water, without addition of any ionic salt.

3.1. Effect of salt addition on mass yield

The mass yield is the fraction of solid product (biochar) that remains after the hydrothermal carbonization (HTC) process, compared to the original dried biomass. In this case mass yield was calculated on a dry ash-free basis, since some of the salt precipitates onto the biochar, as reflected in the ash content. Table 1 shows the mass yields obtained under each condition. Compared to the control with no salt added, the hydrothermal carbonizations with Ca propionate, Ca chloride, or Ca formate added had slightly increased mass yield. This indicates that a lesser proportion of the biomass was removed by HTC when these salts were added. The hydrothermal carbonization with Ca acetate showed the same mass yield as that of the control. The salts Mg acetate, Ca lactate, and Li chloride displayed mass yields lower than the control experiment, indicating greater biomass removal. In HTC, hemicelluloses are removed most rapidly and completely, cellulose is the next most quickly to be solubilized, and lignin is relatively inert [12]. Hemicelluloses and cellulose have lower higher heating values (HHVs) than lignin, so that the more they are removed from the biomass, the greater its HHV. In addition, these lower HHV components may react to form products with increased HHV, particularly in the presence of catalyzing salts [5,6,13].

3.2. Effect of salt addition on energy densification

Energy densification is defined as the ratio of the HHV of the biochar to that of the original raw biomass. Table 1 shows the higher heating value (HHV) calculated on a dry ash free basis, and the energy densification for each experiment. Fig. 1 shows the HHV values for each run and for raw loblolly pine. The control experiment, with no salt added, produced a biochar with HHV increased by 34% relative to the raw feedstock. Ca formate shows a lower densification. Its lower HHV probably correlates to its higher mass yield, which indicates that less hemicelluloses and cellulose is removed from the biomass, leaving a higher proportion of these components compared to lignin. Ca propionate, Ca acetate, and Mg acetate additions show energy densifications similar to the control, thus indicating that these salts neither assist nor hinder the hydrothermal carbonization. Ca lactate, Li chloride, and Ca chloride addition significantly increase the energy densification compared to the control experiment. Chloride ions are known to disrupt the hydrogen bonding between adjacent cellulose polymer strands [14,15], facilitating their solubilization and removal from biomass. The lactate may perform a similar action in disrupting cellulose hydrogen bonding. If more cellulose is removed from the biomass, a higher proportion of lignin remains, increasing the biochar's HHV. The added salts also may catalyze condensation reactions which cause the formation of products with greater HHV, which may precipitate into the biochar pores [6,13].

3.3. Effect of salt addition on energy yield

Energy yield is defined as the product of mass yield and energy densification. It is a measure of the fraction of energy from the raw biomass that remains in the biochar product. Table 1 shows the energy yields from each of the hydrothermal carbonizations. Ca lactate, Ca propionate, Ca acetate, and Ca formate additions give energy yields similar to that of the control experiment. Mg acetate addition to the hydrothermal carbonization process causes somewhat lower energy yield. Ca chloride and Li chloride give surprisingly high energy yields of over 90%. These salts with chloride anions must interact with the biomass so as to remove only low HHV components, while leaving lignin and other high HHV components unchanged, so that mass yield and energy densification are

Table 1

Mass yield, higher heating value (HHV), energy densification, energy yield, pH, ash (wt.%), and reaction pressure for hydrothermal carbonization (HTC) with and without salt addition. Values marked ± indicate 1 standard deviation of triplicate runs. Energy densification ratio is calculated by dividing the dry ash-free HHV of the pretreated biomass by the average dry ash-free HHV of raw pine (18.74 MJ/kg).

Salt added	Mass yield (%)	HHV (MJ/kg)	Densification ratio	Energy yield (%)	pH	Ash (wt.%)	*P* (MPa)
No salt added (control)	59.9 ± 2.9	25.11 ± 0.73	1.34 ± 0.039	80 ± 4	3.05 ± 0.05	0.6 ± 0.4	4.3 ± 0.04
Ca lactate	55.3 ± 4.6	26.94 ± 0.21	1.44 ± 0.011	79 ± 6	3.83 ± 0.04	4.5 ± 0.7	4.0 ± 0.03
$CaCl_2$	61.4 ± 1.0	27.51 ± 0.79	1.47 ± 0.042	90 ± 3	1.63 ± 0.16	7.4 ± 1.5	3.5 ± 0.17
LiCl	60.9 ± 0.9	28.20 ± 1.32	1.50 ± 0.071	92 ± 3	1.76 ± 0.05	9.5 ± 5.2	3.0 ± 0.03
Ca propionate	62.80	24.90	1.33	83	4.84	5.2	3.9
Ca acetate	58.30	25.34	1.35	78	4.64	7.4	4.0
Ca formate	72.80	21.47	1.15	83	4.50	1.3	4.1
Mg acetate	51.70	25.88	1.38	71	4.38	1.9	4.0

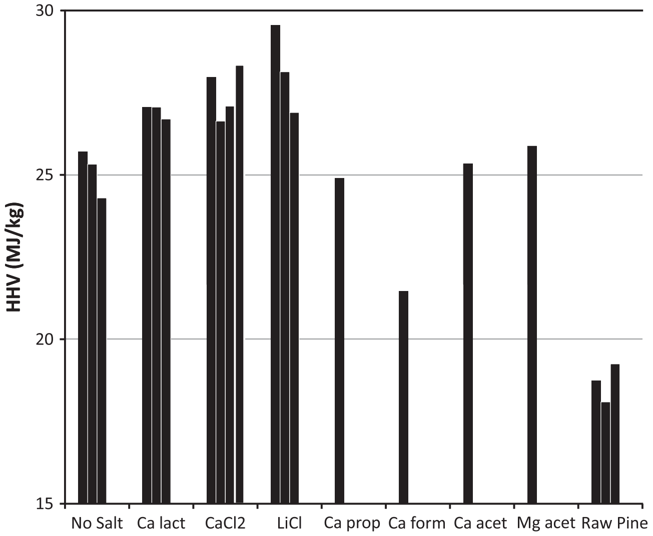

Fig. 1. Higher heating values (HHVs) in of biochar produced by HTC with addition of various salts.

both high. Another possibility is that chloride anions in these salts serve as a catalyst to crosslink lower HHV biomass components into higher fuel value products [6,13–15].

3.3.1. Effect of salt addition on pH

Table 1 shows the pH of the liquid product of the hydrothermal carbonizations. Since the control experiment starts with neutral de-ionized water and produces an acidic solution with pH 2.97, acid is evidently produced by the reaction. HTC has been shown to produce acetic acid, along with smaller amounts of formic and lactic acids [6]. Adding acetate to the reaction scheme may shift equilibrium reactions in which it is involved to the left, so that less acetic acid is formed. This may partially explain the higher pH of the solution resulting from addition of Ca acetate and Mg acetate. Higher pH values could be attributed to anion hydrolysis of carboxylate salts. In general, the added salts, except for those with chloride, buffer the solution such that pH is not decreased as much as would be expected otherwise. The presence of chloride ions from Li chloride and Ca chloride enhance the activity of the H^+ ions, resulting in greatly lowered pH [6]. Of the non-chloride salts, Ca lactate shows the lowest pH, which may indicate a greater extent of reaction, with more acid production.

3.4. Effect of salt addition on reaction pressure

Table 1 displays the pressures for the 260 °C hydrothermal carbonizations, with and without salt addition. As expected, adding salt reduces the reaction pressure. The more hygroscopic salts, Li chloride and Ca chloride, show markedly lower reaction pressure, 30% lower for LiCl and 19% lower for $CaCl_2$. Except for Ca formate, whose pressure reduction is minimal, the other salts reduce pressure by about 7%. Less than 10% of salts remain in the biomass product, so recycling salt solution for reuse in HTC is possible. LiCl and Ca lactate are more expensive than $CaCl_2$. However, in a large-scale process, any cost advantages from reduced pressure may be offset by increased corrosion rates resulting from addition of a chloride salt.

4. Conclusions

Adding Ca lactate, Li chloride, and Ca chloride to the HTC pretreatment of loblolly pine enhances the reactivity resulting in biochar with increased HHV compared to that with no salt added. Inexpensive Ca chloride shows a particularly higher energy yield and a large reduction in hydrothermal carbonization pressure with respect the other non-chloride salts studied. If a Ca salt without chloride is desired, Ca lactate shows high energy densification and some pressure reduction when added to the hydrothermal carbonization process.

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